

Statistical and Low Temperature Physics (PHYS393)

3. Paramagnetic salts and oscillators

Dr Kai Hock

University of Liverpool

Contents

3.1 Paramagnetic salts

3.2 Simple Harmonic Oscillator

3.3 Exercises

Aim

To derive the macroscopic properties of paramagnetic salts and the 3D simple harmonic oscillator.

Objectives

1. To describe the basic physics of a paramagnetic salt.
2. To use the partition function to calculate thermodynamic quantities.
3. To derive the magnetisation of a paramagnetic salt.
4. To explain the use of the 3D simple harmonic oscillator to model thermal vibration.
5. To explain the equipartition theorem.

3.1 Paramagnetic salts

Paramagnets

We have derived the Boltzmann distribution in theory. It has also be widely observed in experiments.

One good example is the measurement on paramagnetism carried out by Warren E. Henry in 1952, at the Naval Research Laboratory in the United States.



He placed salts of chromium, iron or gadolinium in liquid Helium and measured their magnetisation in a magnetic field.

Then he calculated the magnetisation with a formula that is derived using Boltzmann distribution, and found that the results agree very well.

Warren's results, published in Physical Review

On the left is the experimental setup used by Warren. It contains liquid helium to cool down the paramagnetic sample near the bottom.

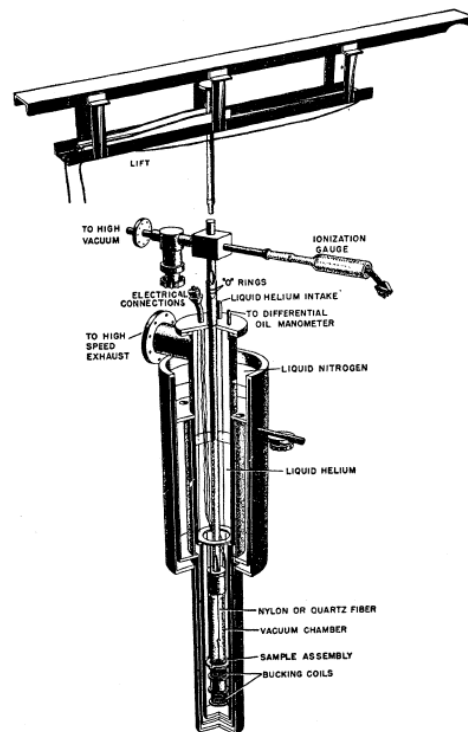


FIG. 1. Schematic diagram of assembly of metal Dewar for liquid helium and sample; displacement lift is shown at top.

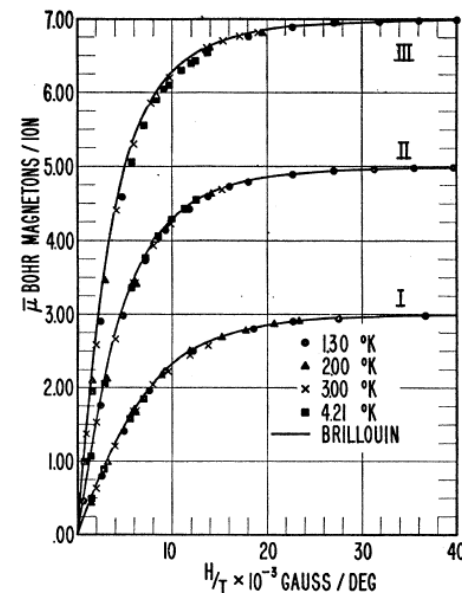


FIG. 3. Plot of average magnetic moment per ion, $\bar{\mu}$ vs H/T for (I) potassium chromium alum ($J=S=3/2$), (II) iron ammonium alum ($J=S=5/2$), and (III) gadolinium sulfate octahydrate ($J=S=7/2$). $g=2$ in all cases, the normalizing point is at the highest value of H/T .

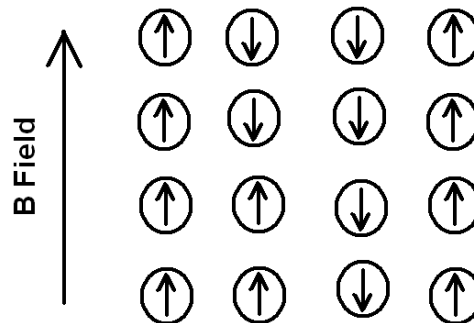
On the right are the measurements and calculations which agree well.

A Spin-1/2 Paramagnet

We shall learn how to do this type of calculation.

As with Warren's experiments, we consider a solid, paramagnetic salt. Such a salt contains ions that have magnetic moments. The magnetic moment in each ion comes from the electrons in the ion.

Consider a salt with an angular momentum of J for each magnetic ion.



A Spin-1/2 Paramagnet

We shall consider the simple case where $J = S = 1/2$. Then the magnetic dipole moment the ion is given by

$$\mu = \mu_B,$$

where μ_B is the Bohr magneton .

The Bohr magneton is a unit of measure for the magnetic moment of the electron. It has the value:

$$\mu_B = 9.274 \times 10^{-24} \text{ J T}^{-1}.$$

Suppose that a magnetic field B is applied to the salt. Since the ion has a magnetic moment, it would have a magnetic potential energy given by

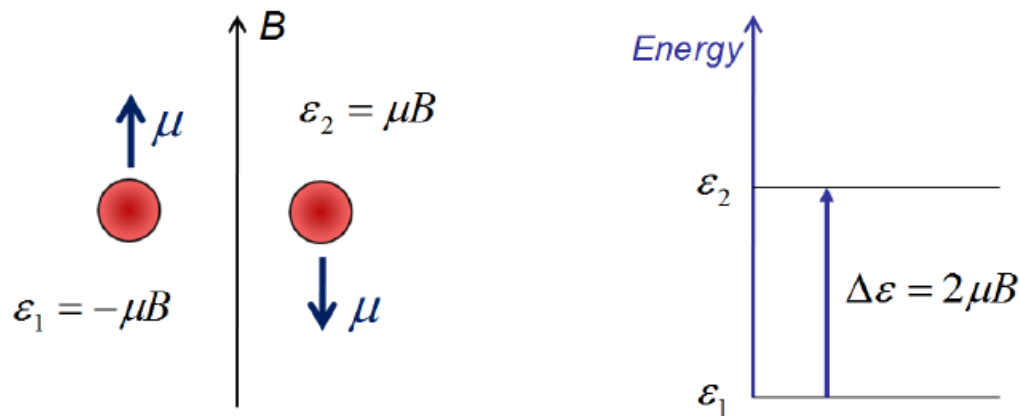
$$\varepsilon = -\mu \cdot \mathbf{B} = -\mu_B B \text{ or } +\mu_B B$$

A Spin-1/2 Paramagnet

The sign of the magnetic potential energy

$$\varepsilon = -\boldsymbol{\mu} \cdot \mathbf{B} = -\mu_B B \text{ or } +\mu_B B$$

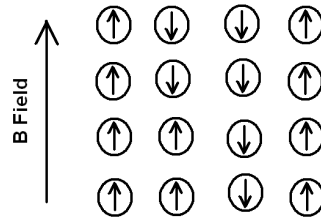
would depend on whether the ion is spin up or spin down, as shown in the figure to the left.



The magnetic field thus splits the energy into 2 levels. We shall call this a spin-1/2 paramagnet.

A Spin-1/2 Paramagnet

In the spin-1/2 paramagnet, some ions are spin up, and others are spin down.



Suppose there are N magnetic ions, with a fraction p spin up and a fraction q spin down.

The magnetisation is then defined by the resultant magnetic moment:

$$M = pN\mu_B - qN\mu_B = N\mu_B(p - q)$$

Our result on the most probable macrostate would suggest that they follow the Boltzmann distribution

$$n_i = A \exp(-\varepsilon_i/k_B T).$$

A Spin-1/2 Paramagnet

Since

$$\varepsilon = -\boldsymbol{\mu} \cdot \mathbf{B} = -\mu_B B \text{ or } +\mu_B B$$

the Boltzmann distribution is

$$n_1 = A \exp(\mu_B B / k_B T) \quad \text{and} \quad n_2 = A \exp(-\mu_B B / k_B T)$$

To simplify the expression, define

$$x = \mu_B B / k_B T.$$

Then rewrite the Boltzmann distribution as

$$n_1 = A e^x \quad \text{and} \quad n_2 = A e^{-x}$$

If the magnetic dipoles follow this distribution, the fractions would be given by

$$p = \frac{n_1}{N} \quad \text{and} \quad q = \frac{n_2}{N}$$

A Spin-1/2 Paramagnet

The fractions are

$$p = \frac{n_1}{N} \quad \text{and} \quad q = \frac{n_2}{N}$$

Using the Boltzmann distribution, the total number is

$$\begin{aligned} N &= n_1 + n_2 \\ &= A(e^x + e^{-x}). \end{aligned}$$

The fraction then becomes

$$p = \frac{e^x}{e^x + e^{-x}}$$

and

$$q = \frac{e^{-x}}{e^x + e^{-x}}$$

A Spin-1/2 Paramagnet

The magnetisation is defined by

$$M = N\mu_B(p - q)$$

Substituting our results on p and q gives

$$\begin{aligned} M &= N\mu_B \left(\frac{e^x}{e^x + e^{-x}} - \frac{e^{-x}}{e^x + e^{-x}} \right) \\ &= N\mu_B \tanh x \end{aligned}$$

Substituting

$$x = \mu_B B / k_B T,$$

we get

$$M = N\mu_B \tanh \left(\frac{\mu_B B}{k_B T} \right).$$

This is the equation for magnetisation that we wanted to find.

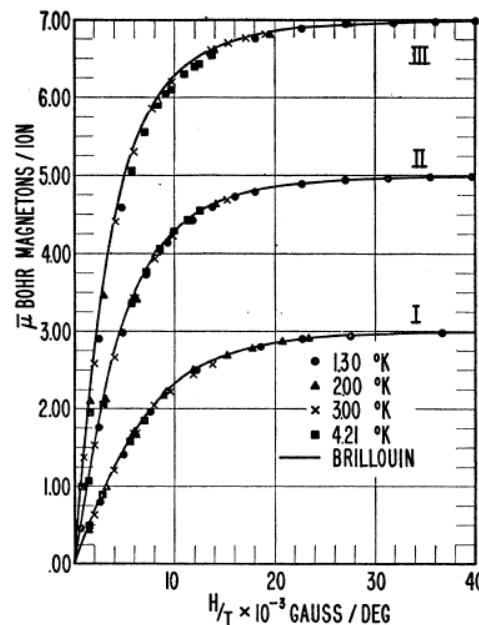
Paramagnets with Angular Momentum J

For paramagnets with momentum J that is more than $1/2$, there would be more than 2 energy levels. The same principles can be used to find the magnetisation, and the result is

$$M = Ng_J\mu_B \left[(J + 1/2) \coth[(J + 1/2)C] - \frac{\coth(C/2)}{2} \right]$$

where $C = g_J\mu_B B/k_B T$ and g_J is the Landé g factor.

This equation gives good agreement with experiments.



We now look at how to apply the Boltzmann distribution to find the heat capacity and entropy of a paramagnetic salt.

The heat capacity behaves in a distinctive way at very low temperatures. The entropy is important for low temperatures cooling techniques. We shall see more of these in the second part of these lectures.

In order to calculate them, it would be useful to develop the method of the partition function.

We shall first develop the method of partition function. This is essentially a series of formulae that will make it easy to calculate various quantities in thermodynamics from the Boltzmann distribution,

$$n_i = A \exp(-\varepsilon_i/k_B T)$$

To see how this works, we start by defining the

$$Z = \sum_i \exp(-\varepsilon_i/k_B T)$$

This is just a sum of the Boltzmann factor over all energy levels of the system that we are interested in. In this case, that would be the paramagnetic salt.

Next, look at the total energy

$$U = \sum_i n_i \varepsilon_i = A \sum_i \varepsilon_i \exp(-\varepsilon_i/k_B T)$$

Compare this with the definition of the partition function Z above. The terms that are summed look similar except for the factor of ε_i .

The idea now is to make a formula that can allow us to calculate the energy U from the partition function Z . Try differentiating the partition function

$$Z = \sum_i \exp(-\varepsilon_i/k_B T)$$

with respect to temperature T . This gives

$$\frac{\partial Z}{\partial T} = \frac{1}{k_B T^2} \sum_i \varepsilon_i \exp(-\varepsilon_i/k_B T)$$

Rearrange the derivative

$$\frac{\partial Z}{\partial T} = \frac{1}{k_B T^2} \sum_i \varepsilon_i \exp(-\varepsilon_i/k_B T)$$

to make the summation the subject:

$$\sum_i \varepsilon_i \exp(-\varepsilon_i/k_B T) = k_B T^2 \frac{\partial Z}{\partial T}$$

We now have the summation part of the energy

$$U = A \sum_i \varepsilon_i \exp(-\varepsilon_i/k_B T)$$

in terms of the partition function Z .

Next, we want to express the factor A in terms of the partition function as well.

Partition Function

To relate A to the partition function, consider the total number of particles:

$$N = \sum_i n_i = A \sum_i \exp(-\varepsilon_i/k_B T)$$

Notice that the summation is just the partition function Z defined above. Therefore

$$N = AZ \quad \text{or} \quad A = N/Z.$$

We can substitute this and the previous result

$$\sum_i \varepsilon_i \exp(-\varepsilon_i/k_B T) = k_B T^2 \frac{\partial Z}{\partial T}$$

into the formula for the energy

$$U = A \sum_i \varepsilon_i \exp(-\varepsilon_i/k_B T).$$

This is the result:

$$U = \frac{Nk_B T^2}{Z} \frac{\partial Z}{\partial T}$$

Notice that in this result

$$U = \frac{Nk_B T^2}{Z} \frac{\partial Z}{\partial T}$$

the total energy is expressed in terms of the partition function.

The reason for doing this is to make it easy to calculate U . In the paramagnetic salts and other systems we shall look at, it is often possible to obtain a fairly simple formula for the partition function, which can then be substituted into the above formula to find the energy U .

We shall see that it is possible to find similar formulae for other quantities, such as entropy, magnetisation and Helmholtz free energy, in terms of the partition function.

The above formula for the energy can also be written as

$$U = Nk_B T^2 \frac{\partial \ln Z}{\partial T}$$

You can check this by differentiating the $\ln Z$.

Next, consider the entropy

$$S = k_B \ln \Omega$$

We want to turn this into a formula in terms of the partition function as well.

In the macrostate (n_1, n_2, \dots) , the number of microstates is given by

$$\Omega = \frac{N!}{\prod_i n_i!}.$$

Applying Stirling's theorem gives:

$$\ln \Omega = N \ln N - N - (n_1 \ln n_1 - n_1) - (n_2 \ln n_2 - n_2) - \dots - (n_i \ln n_i - n_i) - \dots$$

Substituting into the entropy formula above and collecting the terms into a sum gives:

$$S = k_B (N \ln N - \sum_i n_i \ln n_i)$$

To express this

$$S = k_B(N \ln N - \sum_i n_i \ln n_i)$$

in terms of the partition function, start by substituting the Boltzmann distribution:

$$n_i = A \exp(-\varepsilon_i/k_B T)$$

This gives

$$\begin{aligned} S &= k_B[N \ln N - \sum_i n_i (\ln A - \varepsilon_i/k_B T)] \\ &= Nk_B \ln N - k_B \ln A \sum_i n_i + \frac{1}{T} \sum_i n_i \varepsilon_i \end{aligned}$$

The sums in the 2nd and 3rd terms are respectively the total number of particles N and energy U . Therefore

$$S = Nk_B \ln N - Nk_B \ln A + \frac{U}{T}.$$

We have obtained

$$S = Nk_B \ln N - Nk_B \ln A + \frac{U}{T}.$$

Recall that we already have the formulae for N and U in terms of the partition function:

$$N = AZ \quad \text{and} \quad U = Nk_B T^2 \frac{\partial \ln Z}{\partial T}$$

Substituting these, we get

$$\begin{aligned} S &= Nk_B \ln AZ - k_B N \ln A + Nk_B T \frac{\partial \ln Z}{\partial T} \\ &= Nk_B \ln Z + Nk_B T \frac{\partial \ln Z}{\partial T} \end{aligned}$$

This is the formula for S in terms of the partition function Z .

We would need one more formula, for the Helmholtz free energy:

$$F = U - TS.$$

We shall first review the results that we are going to use. From thermodynamics, we know that

$$TdS = dU + pdV.$$

where TdS is the heat absorbed by a system, dU the increase in internal energy, and pdV the work done by expanding against an external pressure.

Taking the differential of the Helmholtz free energy:

$$dF = dU - d(TS)$$

and substituting for dU from the previous equation gives:

$$dF = TdS - pdV - d(TS).$$

Simplifying, we get

$$dF = -SdT - pdV.$$

This equation makes it convenient to think of F as a function of T and V . We know from partial differentiation that the differential of the function $F(T, V)$ is

$$dF = \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV$$

Comparing this with the previous equation, we see for example that

$$\left(\frac{\partial F}{\partial V}\right)_T = -p.$$

Partition Function

We have found that the relation

$$\left(\frac{\partial F}{\partial V}\right)_T = -p.$$

So if we can express the Helmholtz free energy F in terms of the partition function, we can use it to find the pressure p . This example would be useful later on in the lectures on ideal gas.

We have previously obtained the formulae for U and S in terms of the partition function:

$$U = Nk_B T^2 \frac{\partial \ln Z}{\partial T}$$

$$S = Nk_B \ln Z + Nk_B T \frac{\partial \ln Z}{\partial T}$$

Substituting these into the definition for Helmholtz free energy:

$$F = U - TS,$$

we obtain

$$F = -Nk_B T \ln Z.$$

Formulae related to the partition function

Boltzmann distribution

$$n_i = A \exp \left(-\frac{\varepsilon_i}{k_B T} \right)$$

Partition function

$$Z = \sum_i \exp \left(-\frac{\varepsilon_i}{k_B T} \right)$$

Total number of particles

$$N = AZ$$

Total energy

$$U = Nk_B T^2 \frac{\partial \ln Z}{\partial T}$$

Entropy

$$S = Nk_B \ln Z + Nk_B T \frac{\partial \ln Z}{\partial T}$$

Helmholtz free energy

$$F = -Nk_B T \ln Z$$

Thermodynamics of the spin-1/2 paramagnet

We can now find the internal energy spin-1/2 paramagnet.

For the spin-1/2 salt, the energy levels are $-\mu_B B$ and $+\mu_B B$. So the partition function is

$$Z = \sum_i \exp\left(-\frac{\varepsilon_i}{k_B T}\right) = \exp\left(\frac{\mu_B B}{k_B T}\right) + \exp\left(-\frac{\mu_B B}{k_B T}\right)$$

This can be written as

$$Z = 2 \cosh\left(\frac{\mu_B B}{k_B T}\right).$$

To find the internal energy, the formula is

$$U = N k_B T^2 \partial \ln Z / \partial T$$

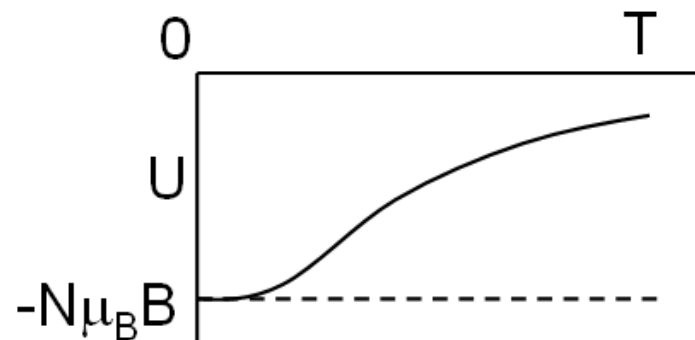
Substituting the above expression for the partition function gives

$$U = -N \mu_B B \tanh\left(\frac{\mu_B B}{k_B T}\right).$$

Behaviour of the internal energy

The behaviour of the internal energy at high or low temperatures gives insight into the physics of the paramagnet.

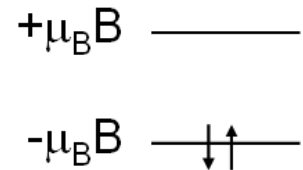
$$U = -N\mu_B B \tanh\left(\frac{\mu_B B}{k_B T}\right).$$



When U is plotted against T , the graph goes to $-N\mu_B B$ for small T , and zero for large T .

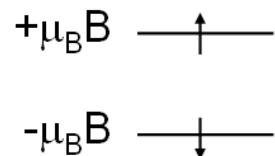
Can we explain this physically?

At low temperature, most atoms would be in the ground state
- the lower energy level $-\mu_B B$.



The total energy would be N times this, which is $-N\mu_B B$.

At high temperature, the difference between the energy levels $2\mu_B B$ would be small compared with the $k_B T$ in $\exp(-\epsilon/k_B T)$.



So the levels would be nearly equally populated: half at $-\mu_B B$, half at $+\mu_B B$. The total would go to zero.

The heat capacity

We have previously obtained the energy

$$U = -N\mu_B B \tanh\left(\frac{\mu_B B}{k_B T}\right).$$

We can obtain the heat capacity by differentiating with respect to temperature T :

$$C = \frac{dU}{dT}.$$

This gives:

$$C = Nk_B \left(\frac{\mu_B B}{k_B T}\right)^2 \operatorname{sech}^2\left(\frac{\mu_B B}{k_B T}\right).$$

For high temperature - i.e. when $k_B T$ is large compared with $\mu_B B$ - the argument in the hyperbolic secant function becomes small:

$$\frac{\mu_B B}{k_B T} \rightarrow 0,$$

and so the hyperbolic secant tends to 1:

$$\operatorname{sech} \left(\frac{\mu_B B}{k_B T} \right) \rightarrow 1.$$

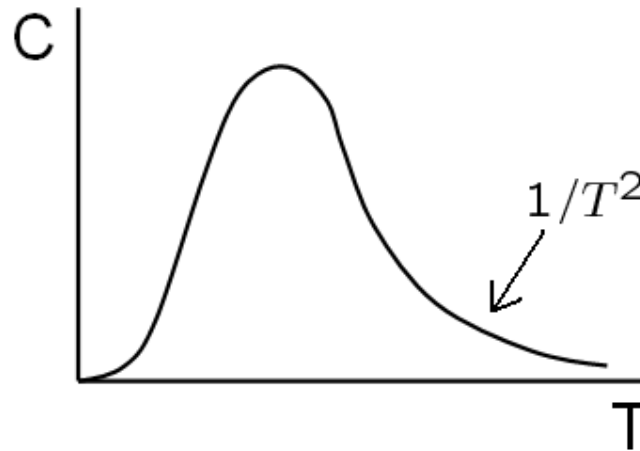
So at high temperature the heat capacity becomes

$$C \rightarrow N k_B \left(\frac{\mu_B B}{k_B T} \right)^2$$

which is proportional to $1/T^2$.

The heat capacity

The graph of the heat capacity shows a peak. Beyond the peak, the graph falls off as $1/T^2$. Both features are characteristic of the magnetic energy levels.



We shall learn later that heat capacities usually increases. So having a peak is unusual. For this reason, the peak is called the Schottky anomaly.

Note that when we say "high temperature" here, it is relative to the magnetic energy levels. The Schottky anomaly typically occurs around 1 K.

The entropy.

Recall that there is also a formula to derive the entropy from the partition function.

$$S = Nk_B \ln Z + Nk_B T \frac{\partial \ln Z}{\partial T}$$

Substituting the partition function

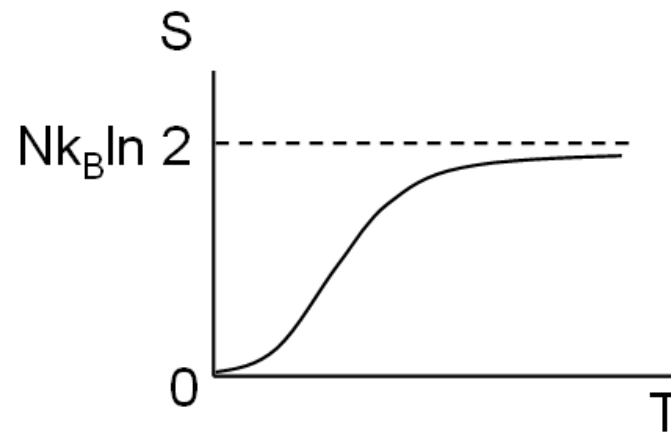
$$Z = 2 \cosh(\mu_B B / k_B T)$$

we get the entropy for the spin-1/2 salt:

$$S = Nk_B \ln \left[2 \cosh \left(\frac{\mu_B B}{k_B T} \right) \right] - \frac{N\mu_B B}{T} \tanh \left(\frac{\mu_B B}{k_B T} \right).$$

The entropy.

The graph for the entropy looks like this:

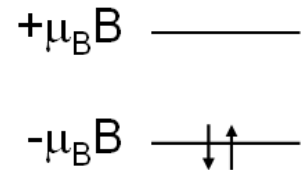


Again, we would be interested in the high and low temperature behaviours.

Recall the formula for entropy: $S = k_B \ln \Omega$.

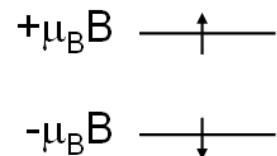
Behaviour of the entropy

At low temperature, most atoms would be in the ground state.



There is only 1 way to arrange this. So the entropy would tend to $S = k_B \ln 1 = 0$.

At high temperature, the difference between the energy levels would be small compared with the $k_B T$ in $\exp(-\epsilon/k_B T)$.



The atom is equally likely to be in either level. There are 2 possible arrangements for each of the N atoms - 2^N in total.

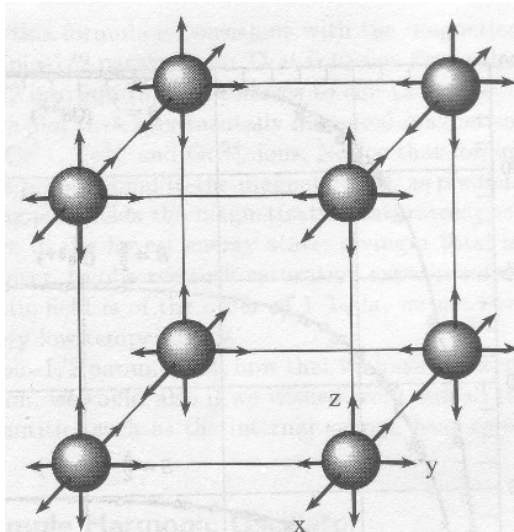
So the entropy would tend to $S = k_B \ln 2^N = Nk_B \ln 2$.

3.2 Simple Harmonic Oscillator

The Simple Harmonic Oscillator

The Simple Harmonic Oscillator is one of the early attempts to understand the heat capacity of solids using quantum mechanics.

It was proposed by Einstein. The idea is to think of - to model - a solid as atoms vibrating independently of one another other.



Glazer and Wark (2001)

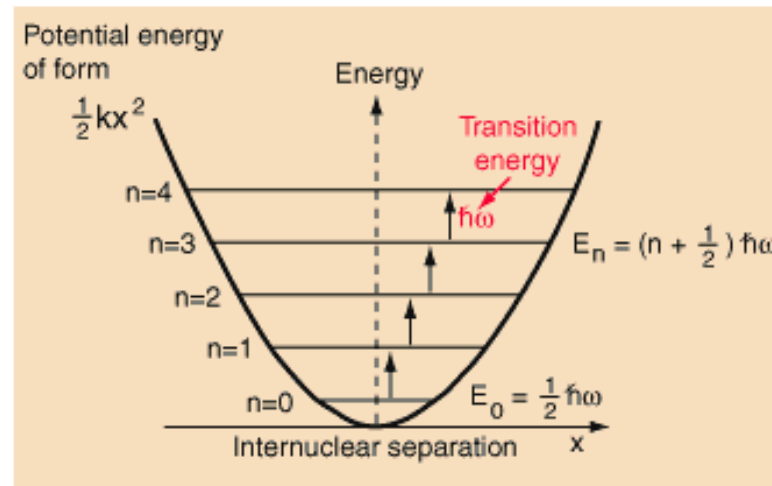
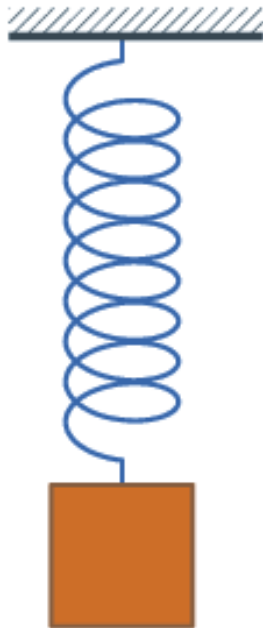
Each atom sits in its own potential well. It could undergo simple harmonic oscillation in all 3 directions x , y and z . Vibration in any one direction is independent of vibration in the other two directions.

The 1-D case

From quantum mechanics, we know that the energy for a 1-D simple harmonic oscillator is

$$\varepsilon_n = (n + 1/2)h\nu.$$

where n is an integer, and ν is the frequency.



<http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/hosc.html>

The 1-D case

The energy

$$\varepsilon_n = (n + 1/2)h\nu.$$

can be substituted into the partition function

$$Z = \sum_i \exp(-\varepsilon_i/k_B T)$$

This gives

$$\begin{aligned} Z_{1D} &= \sum_n \exp(-(n + 1/2)h\nu/k_B T) \\ &= \frac{\exp(-h\nu/2k_B T)}{1 - \exp(-h\nu/k_B T)} \end{aligned}$$

The energy can then be found using this formula:

$$U = Nk_B T^2 \frac{\partial \ln Z_{1D}}{\partial T}$$

The 1-D case

Using the partition function, we obtain the formula for the energy:

$$U = \frac{Nh\nu}{2} + \frac{Nh\nu}{\exp(h\nu/k_B T) - 1}$$

We are often interested in materials at high and low temperatures, because the behaviour can get simpler.

To obtain the high temperature limit for the energy, note that the exponential function:

$$e^x \rightarrow 1 + x$$

for small x . For high T ,

$$\exp\left(\frac{h\nu}{k_B T}\right) \rightarrow 1 + \frac{h\nu}{k_B T}$$

Substituting into the above formula for U gives

$$U = \frac{Nh\nu}{2} + Nk_B T$$

We have obtained

$$U = \frac{N h \nu}{2} + N k_B T$$

The first term on the right is a constant. The second term increases with temperature T . So for high T , the first term can be neglected, and we get the high temperature limit for the energy:

$$U \rightarrow N k_B T \quad \text{as} \quad T \rightarrow \infty.$$

The quantity that can be directly measured in an experiment is the heat capacity. This can be obtained by differentiating U :

$$C = \frac{dU}{dT}$$

Differentiating the energy

$$U = \frac{Nh\nu}{2} + \frac{Nh\nu}{\exp(h\nu/k_B T) - 1}$$

with respect to temperature gives the heat capacity:

$$C = Nk_B \left(\frac{\theta}{T} \right)^2 \frac{\exp(\theta/T)}{(\exp(\theta/T) - 1)^2}$$

where $\theta = h\nu/k_B$.

We now need to extend this to a real material, which is 3-D.

The 3-D case

In the 3-D case, the motion in x , y and z are assumed to be independent of one another.

This means that the energy can be obtained by simply adding up the energy in each direction, or multiplying the 1-D energy by 3. Likewise for the heat capacity.

The 1-D heat capacity is:

$$C = Nk_B \left(\frac{\theta}{T} \right)^2 \frac{\exp(\theta/T)}{(\exp(\theta/T) - 1)^2}$$

where $\theta = h\nu/k_B$.

So we simply insert a factor of 3 and get the 3-D heat capacity:

$$C_{3D} = 3Nk_B \left(\frac{\theta}{T} \right)^2 \frac{\exp(\theta/T)}{(\exp(\theta/T) - 1)^2}$$

The 3-D heat capacity is:

$$C_{3D} = 3Nk_B \left(\frac{\theta}{T}\right)^2 \frac{\exp(\theta/T)}{(\exp(\theta/T) - 1)^2}$$

We would be interested in the high temperature behaviour. Using the previous method, when T is large,

$$\exp\left(\frac{\theta}{T}\right) \approx 1 + \frac{\theta}{T}$$

The above formula becomes

$$C_{3D} = 3Nk_B \left(\frac{\theta}{T}\right)^2 \frac{1 + \theta/T}{(\theta/T)^2} = 3Nk_B \left(1 + \frac{\theta}{T}\right)$$

For large T , θ/T in the bracket would be a lot smaller than 1, so

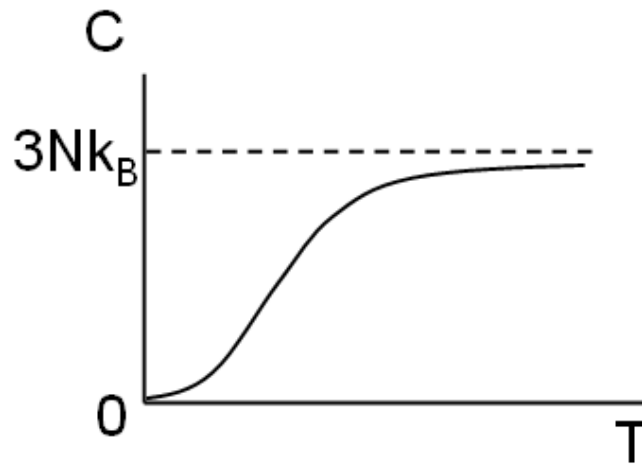
$$C_{3D} \rightarrow 3Nk_B \quad \text{as} \quad T \rightarrow \infty.$$

The heat capacity

Using the formula we have obtained:

$$C_{3D} = 3Nk_B \left(\frac{\theta}{T} \right)^2 \frac{\exp(\theta/T)}{(\exp(\theta/T) - 1)^2}$$

we can sketch the graph for the heat capacity. It looks like this:

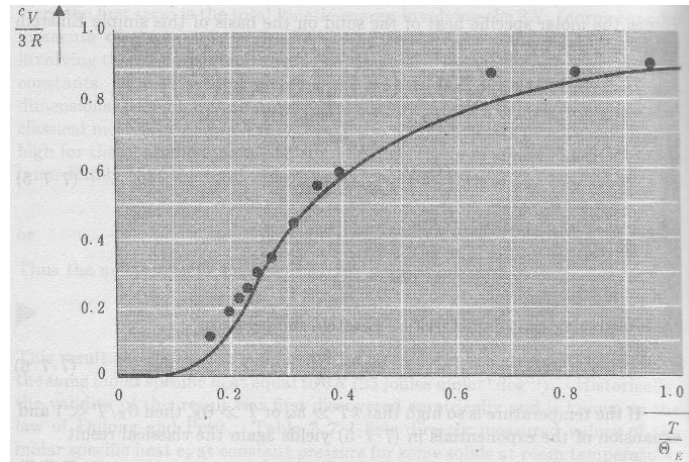


As we have just shown, the heat capacity approaches $3Nk_B$ at high T .

This agrees with the empirical Law of Dulong and Petit, who measured many solids at room temperature in 1819.

Compare with experiment

It also agrees with experiment at lower temperature.



A. Einstein, Ann. Physik, vol. 22, p. 186 (1907)

However, when the temperature gets too low, it falls off exponentially.

This does not agree with experiments, which show that $C \propto T^3$.

This is because the effects of co-ordinated movements among atoms become important. A new model using phonons is needed. We shall learn about this later.

The equipartition theorem

We have seen that at high temperature, the heat capacity approaches $3Nk_B$.

This can be understood this using the "equipartition theorem," which states that:

"The mean value of each independent quadratic term in the energy is equal to $\frac{1}{2}k_B T$."

In our case, "quadratic term" refers to the kinetic energy $\frac{1}{2}mv^2$, or the potential energy of the harmonic oscillator, $\frac{1}{2}kx^2$.

We can prove this by finding, for example, the mean kinetic energy in the Boltzmann distribution:

$$\frac{\int \frac{1}{2}mv^2 \exp(-\frac{1}{2}mv^2/k_B T) dv}{\int \exp(-\frac{1}{2}mv^2/k_B T) dv} = \frac{1}{2}k_B T$$

Explaining the Dulong and Petit Law

The equipartition theorem can help us to understand the Dulong and Petit Law - that the heat capacity is $3Nk_B$ at high temperature.

There are N atoms.

Each atom vibrates in 3 directions.

In each direction, there is kinetic energy and potential energy.

Each type of energy has a mean value of $\frac{1}{2}k_B T$.

The total is $U = N \times 3 \times 2 \times \frac{1}{2}k_B T = 3Nk_B T$.

Therefore, the heat capacity is $C = U/T = 3Nk_B$.

1. The distinguishable particles model of the paramagnetic ions in a solid gives a good description of the magnetisation.
2. The partition function is given by $Z = \sum_i \exp(-\epsilon_i/k_B T)$. This can be used to derive quantities like energy, heat capacity, entropy, ...
3. We can often explain the behaviour of these quantities at high or low temperature physically, in a simple way.
4. The simple harmonic oscillator model of a solid gives a good description of the heat capacity, except at very low temperature.

3.3 Exercises

Exercise 1

Given that the total energy of a system is

$$U = A \sum_i \varepsilon_i \exp(-\varepsilon_i/k_B T)$$

where A is defined by the normalisation from

$$N = A \sum_i \exp(-\varepsilon_i/k_B T)$$

demonstrate that

$$U = N k_B T^2 \frac{\partial \ln Z}{\partial T}$$

where

$$Z = \sum_i \exp(-\varepsilon_i/k_B T)$$

Answer

First, note that since $Z = \sum \exp(-\varepsilon_i/k_B T)$

$$N = A \sum_i \exp(-\varepsilon_i/k_B T) = AZ$$

Next,

$$\frac{\partial \ln Z}{\partial T} = \frac{1}{Z} \frac{\partial Z}{\partial T} = \frac{1}{Z} \sum \frac{\varepsilon_i}{k_B T^2} \exp(-\varepsilon_i/k_B T)$$

Multiplying the two equations above,

$$N \frac{\partial \ln Z}{\partial T} = \frac{A}{k_B T^2} \sum \varepsilon_i \exp(-\varepsilon_i/k_B T)$$

Rearranging,

$$Nk_B T^2 \frac{\partial \ln Z}{\partial T} = A \sum \varepsilon_i \exp(-\varepsilon_i/k_B T)$$

which is U . Therefore

$$Nk_B T^2 \frac{\partial \ln Z}{\partial T} = U$$

Exercise 2

The total energy of a paramagnet is

$$U = -N\mu_B B \tanh(\mu_B B/k_B T)$$

Show that the heat capacity is given by

$$C = Nk_B \left(\frac{\theta}{T}\right)^2 \frac{\exp(\theta/T)}{(\exp(\theta/T) + 1)^2}$$

where $\theta = 2\mu_B B/k_B$

Show that the limiting form at high temperature is

$$C = \frac{Nk_B}{4} \left(\frac{\theta}{T}\right)^2$$

and at low temperature is

$$C = Nk_B \left(\frac{\theta}{T}\right)^2 \exp(-\theta/T)$$

Answer 2

The heat capacity is obtained by differentiating
 $U = -N\mu_B B \tanh(\mu_B B/k_B T)$:

$$C = \frac{dU}{dT} = -N\mu_B B \left(\frac{-\mu_B B}{k_B T^2} \right) \left[\cosh \left(\frac{\mu_B B}{k_B T} \right) \right]^{-2}$$

In terms of $\theta = 2\mu_B B/k_B$,

$$\begin{aligned} C &= Nk_B \left(\frac{\theta}{2T} \right)^2 \left[\cosh \left(\frac{\theta}{T} \right) \right]^{-2} \\ &= Nk_B \left(\frac{\theta}{2T} \right)^2 \frac{4}{(\exp(\theta/2T) + \exp(-\theta/2T))^2} \\ &= Nk_B \left(\frac{\theta}{T} \right)^2 \frac{1}{(\exp(\theta/2T) + \exp(-\theta/2T))^2} \frac{\exp(\theta/T)}{\exp(\theta/T)} \\ &= Nk_B \left(\frac{\theta}{T} \right)^2 \frac{\exp(\theta/T)}{(\exp(\theta/T) + 1)^2} \end{aligned}$$

Some exercises

At high temperature, $\exp(\theta/T) \rightarrow 1$.

$$\begin{aligned} C &= Nk_B \left(\frac{\theta}{T}\right)^2 \frac{\exp(\theta/T)}{(\exp(\theta/T) + 1)^2} \\ &\rightarrow Nk_B \left(\frac{\theta}{T}\right)^2 \frac{1}{(1 + 1)^2} \\ &= \frac{Nk_B}{4} \left(\frac{\theta}{T}\right)^2 \end{aligned}$$

At low temperature, $\exp(\theta/T) + 1 \rightarrow \exp(\theta/T)$.

$$\begin{aligned} C &= Nk_B \left(\frac{\theta}{T}\right)^2 \frac{\exp(\theta/T)}{(\exp(\theta/T) + 1)^2} \\ &\rightarrow \left(\frac{\theta}{T}\right)^2 \frac{\exp(\theta/T)}{\exp(\theta/T)^2} \\ &= Nk_B \left(\frac{\theta}{T}\right)^2 \exp(-\theta/T) \end{aligned}$$